SOME ELECTRICAL PROPERTIES OF SELENIUM.

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III. THE INFLUENCE OF TEMPERATURE UPON THE RECOVERY.

IN earlier papers the writer described experiments dealing with the change in conductivity of selenium under the action of light and of X-rays, and in particular with the effect upon the recovery of a variation in the wave-length of the exciting light, the intensity of excitation, and the duration of exposure. In the present paper are described some further experiments to show the change in the resistance of a selenium cell and the form of the resulting recovery curve produced by (1) a sudden increase in temperature; (2) exposure to light at low temperatures.

THE EFFECT OF CHANGE IN TEMPERATURE.

It was early noted that an increase of temperature acts upon selenium as does light to produce an increase in the conductivity. Bidwell from the study of some half dozen cells concluded that for each cell there is a temperature at which the resistance is a maximum and that for the cells studied the temperature of maximum resistance ranged from 14° C. to 30° C.[1] The sensitiveness of the cell towards light has been shown, furthermore, to decrease with an increase in temperature,[2] *i. e.*, to depend upon the resistance.[3] K. Aichi and T. Tanakadate[4] in their study of the influence of temperature upon the electrical conductivity of selenium found that if a cell be warmed and cooled from different temperatures, the conductivity describes a curve without returning to the point of starting and that the final value of the conductivity is higher than the initial value. Pochettino and Trabacchi[5] concluded as a result

[1] Bidwell, Phil. Mag., Vol. 11, p. 302.

[2] R. Marc, Zeits. für anorgan. Chem., Vol. 37, p. 459.

[3] Brown and Stebbins, PHYS. REV., Vol. 26, p. 273.

[4] Aichi and Tanakadate, Tokyo K., Vol. 2, p. 217; Beib., Vol. 29, p. 997.

[5] Pochettino and Trabacchi, N. Cim., Ser. 5, Vol. 13, p. 286.

of many experiments that cells which at ordinary temperatures have a high resistance and decrease in resistance when lighted also decrease in resistance when heated but when cooled do not return to the initial resistance for from twelve to twenty-four hours. Repetition of this changing thermal treatment lowers the resistance and the light sensitiveness and causes the hysteresis to vanish, but after some time the cells resume the original resistance.

In any study of the effect of temperature upon the resistance of selenium it is necessary to distinguish between a change in temperatures possibly not exceeding 100°C. and the effect of prolonged heating at a temperature sufficiently high to bring about an allotropic transformation, which would permanently alter the conductivity and the light sensitiveness. In the present experiments the effect of changes in temperature below 100° C. was considered in order to determine whether the action of light and heat in producing a change in conductivity is the same. If light and heat set up within the cell exactly the same process then the recovery following a return to the initial condition after a sudden increase in light or heat should be of the same type, *i. e.*, the recovery curves should be of the same form.

In the temperature experiments there were used two small home-made cells of the Bidwell type with a sensitive surface about 5×2 cm. in area, mounted by inserting each end in a rectangular block of wood 3×2 cm. in area. The cell thus mounted was enclosed with a calcium chloride drying tube in a tin box just large enough to admit the wooden supports. The terminals were led out through a tube about 20 cm. long, the end of which was plugged with soft wax. The face of the cell so mounted was within about 5 cm. of the wall of the box that it might quickly attain the temperature of the surrounding bath.

The method followed was to plunge the box containing the cell in melting ice and keep it there until the resistance attained a steady value. As in the previous experiments the resistance was measured by making the cell one arm of a Wheatstone bridge balanced for a resistance approximately equal to the mean resistance of the cell and calibrated by the substitution for the cell of known resistances. By this means there was obtained a calibration curve which gave the resistance of the cell corresponding to any galvanometer deflection. After the resistance at 0° C. had been ascertained the cell was transferred to boiling water and left for periods ranging from ten minutes to two hours until the resistance ceased to decrease appreciably. It was then quickly replaced in the ice-bath and left to

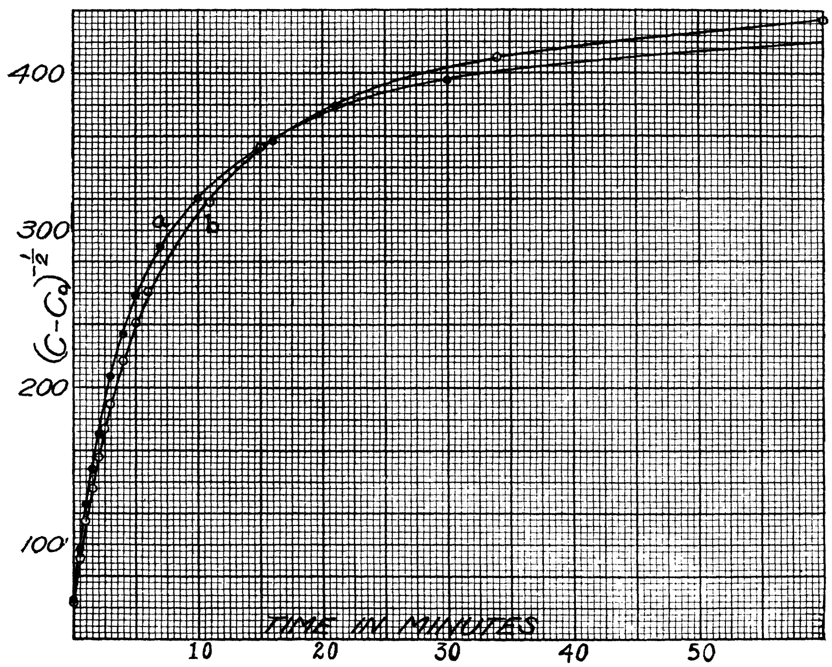

Fig. 1.

Recovery of normal 0° resistance after an increase in temperature of 100°.[1] Cell XVII. Time in 100° bath: *a*, 10 minutes; *b*, 2 hours. Initial 0° resistance: *a*, 103,000; *b*, 97,000.

return to the normal 0° C. resistance. During the recovery the resistance was noted at frequent intervals. From the data so obtained curves were plotted, as in the earlier experiments, with the reciprocal square roots of the changes in conductivity as ordinates and the times as abscissæ. The resulting curves are shown in Figs. 1 and 2. In form the curves are similar to those obtained for the

[1]For these curves additional points were located as follows: *a*, 1°30′, 439, 2°25′, 463, 3°45′, 483; *b*, 1°, 434, 1°30′, 454, 2°, 467.

recovery from excitation by light, with two parts of slight curvature separated by a region of abrupt change of curvature. It is to be noted, however, that in two respects the experiments are not strictly analogous. In the case of recovery from light the contrast was between light and complete darkness, whereas in the case of temperature it is between two temperatures more or less far apart. Furthermore, the return to darkness was almost instantaneous, whereas the temperature change was of necessity gradual. Since the cell required several minutes to attain the temperature of the

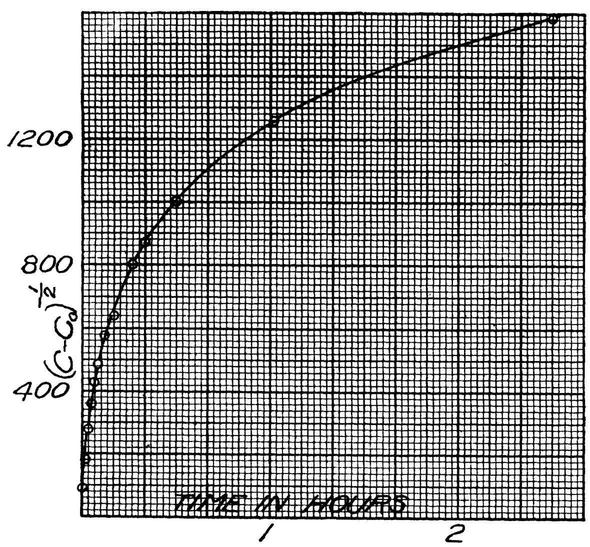

Fig. 2.

Recovery of normal 0° resistance after an increase in temperature of 100°. Cell XVIII. Time in 100° bath, 20 minutes. Initial 0° resistance, 290,000.

bath too great significance cannot be attached to the first part of the curves. It is apparent, however, that heat acts to increase the conductivity in the same way as light. These results partially explain the variation in the normal dark resistance of the cells and also the fact that at a temperature of 100° C. the cells are scarcely at all sensitive to light.

The Action of Light at Low Temperatures.

Since the effect of heat and light upon the selenium cells is the same and the sensitiveness of the cells to light depends upon the resistance, however conditioned, it seems probable that at low temperatures the sensitiveness of the cells would be enormously increased. It was to test this conclusion that the following experiments were undertaken.

The action of light upon selenium at the temperature of liquid air had already been investigated by Pochettino,[1] who found that the dark resistance of his cell decreased from 31,000 ohms at ordinary temperatures to 2,600 ohms at the liquid air temperature while the values of the ratio of the change in resistance to the normal dark resistance were respectively 0.4 and 0.3. Brown and Stebbins,[2] on the contrary, state that the cells used by them were not tested at the liquid air temperature for the reason that the selenium cracked.

In the first of the following experiments comparison was made between the recovery at room temperature, at 0° C., and at the liquid air temperature. Later experiments were made at two intermediate temperatures, about $-90°$ C. and $-65°$ C. For the experiments at the liquid air temperature the cell XVII, used in the temperature experiments, was placed upon a glass plate supported about 2 cm. above the bottom of a glass beaker containing phosphorus pentoxide. The beaker was covered with a thin glass plate sealed with shellac, through which ran the terminal wires. The beaker, enclosed in black paper, was supported by a tight-fitting wooden ring which acted as cover for the Dewar bulb containing liquid air (see Fig. 3). The cell was excited by the light of an acetylene flame placed above the beaker, separated from it by a diaphragm with a circular opening which varied from .6 to 1.2 cm. in diameter and which could be closed by a sliding shutter. This opening could also be covered with a colored glass plate if desired. For the experiments at $-90°$ and $-65°$ the beaker was slipped into a tight-fitting cylinder of tin which extended into

[1] Pochettino, Rend. R. Accad. dei Linc., Ser. 5, Vol. 11, 1 Sem., p. 286.

[2] Brown and Stebbins, Phys. Rev., Vol. 26, p. 273.

the liquid air. The temperature was regulated by the distance the beaker fitted into the cylinder and by the distance the cylinder dipped into the liquid air. By this means the temperature of the cell could be kept constant within 5° or 10° as indicated by a thermometer sealed in through a hole in the glass plate covering the beaker. As the thermometer was found to be unreliable for temperatures below −100° no readings were secured between that temperature and the liquid air temperature. In no case was the cell excited without a rest of at least twenty-four hours in the dark. For the experiments at ordinary temperatures the same apparatus was used, that the conditions might be as nearly uniform as possible.

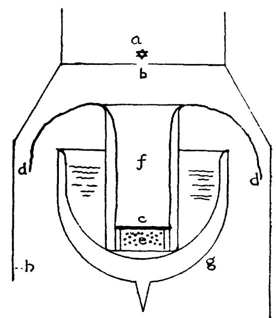

Fig. 3.

a, Acetylene flame; *b*, circular aperture; *c*, cell; *d*, terminal wires; *e*, phosphorus pentoxide; *f*, beaker; *g*, Dewar bulb; *h*, screens.

The method followed was to lower the cell into the liquid air and leave it from thirty minutes to four hours before excitation. Sometimes the cell was left on open circuit and sometimes on closed circuit, with no apparent effect on the results. The resistance of the cell was found to increase so enormously as to be entirely beyond the range of calibration of the bridge. Hence in the later experiments the resistance was measured roughly by balancing the Wheatstone bridge. That this method was far from accurate is evident from the following figures which give the values of the resistances in the three arms of the bridge and the calculated resistance of the cell in a typical instance.

500,000 : 200 = x : 100,000	x = 250 megohms.
1,000,000 : 480 = x : 200,000	x = 417 "
500,000 : 130 = x : 100,000	x = 385 "
1,000,000 : 240 = x : 100,000	x = 417 "
250,000 : 80 = x : 80,000	x = 250 "

While these results differ widely it is to be noted that they are of the same order of magnitude and from the method of plotting it is evident that the curves would not depart appreciably from the correct form if the resistance were assumed to be infinite.

After the cell had been thus cooled and its resistance measured it was excited in the manner already indicated for 10 sec. in the earlier experiments and for a time sufficient to produce saturation

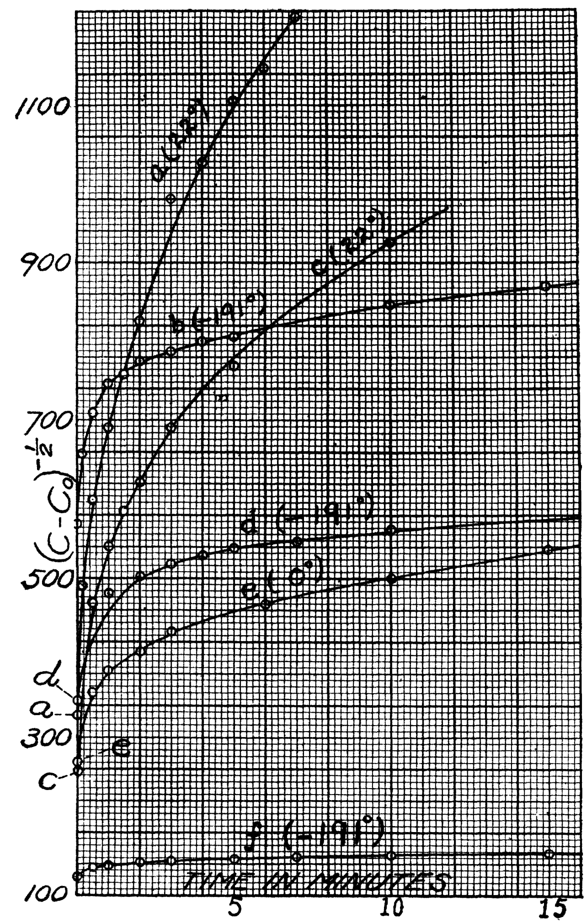

Fig. 4.

Variation in rate of recovery from excitation by light at different temperatures and intensities. Cell XVII. Red light excitation, *a*, Diameter of aperture, 0.6 cm.; time of excitation, 10 sec.; initial dark resistance, 64,000 ohms; *b*, diameter of aperture 0.6 cm., time of excitation 10 sec., initial dark resistance 4×10^8 ohms;[1] *c*, diameter of aperture 0.9 cm., time of excitation 10 sec., initial dark resistance 71,700 ohms; *d*, diameter of aperture 0.9 cm., time of excitation 10 sec., initial dark resistance 4×10^8 ohms;[1] *e*, diameter of aperture 0.6 cm., time of excitation, to saturation, initial dark resistance 92,500 ohms; *f*, diameter of aperture 0.6 cm., time of excitation, to saturation, initial dark resistance 4×10^8 ohms.

[1]Resistance assumed from later experiments with this cell.

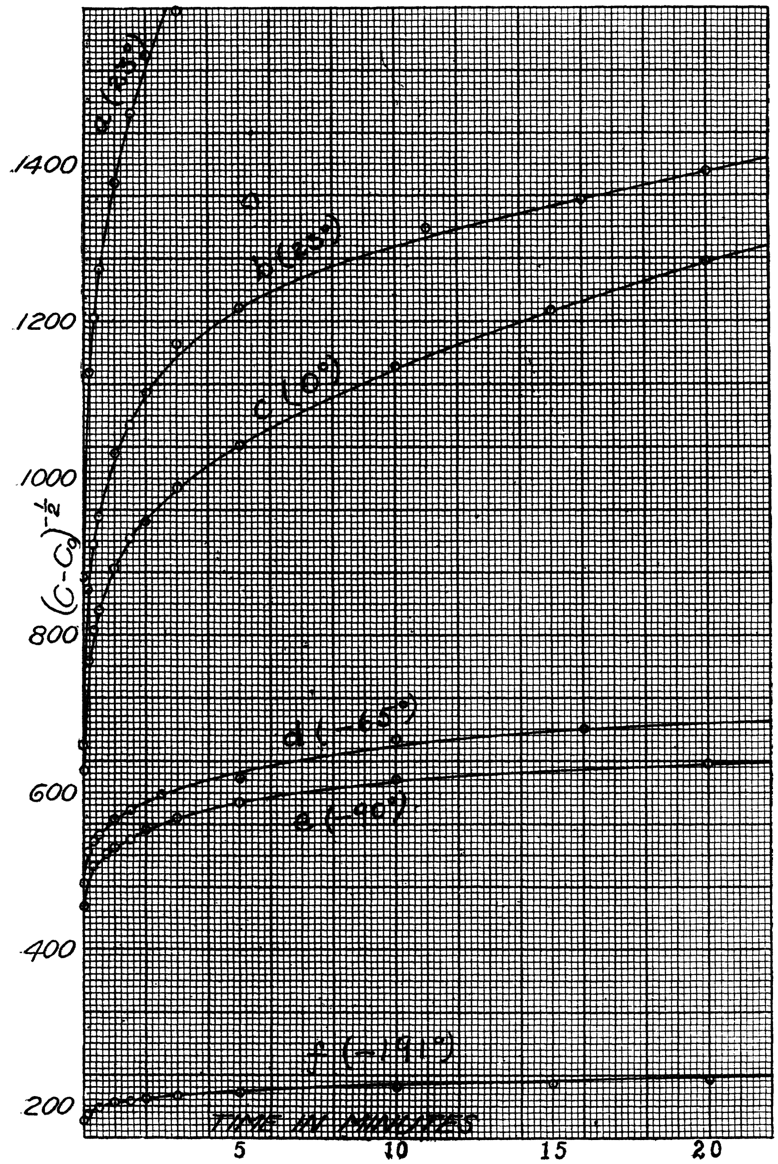

Fig. 5.

Variation in rate of recovery from excitation by light at different temperatures. Excitation to saturation. *a*, *d*, *e*, Cell XXI.; white light through aperture 0.9 cm. in diam.; initial dark resistances: 292,000; 3.6×10^6; 9×10^6. *b*, *c*, *f*, Cell XIX.; red light excitation, aperture 0.6 cm.; initial dark resistances: 209,500; 417,000; 2×10^9.

in the later experiments. The instant the light was turned on the resistance began to decrease at so extremely rapid a rate that for the first few seconds it was impossible to follow the change by the galvanometer method used. By the time approximate saturation was reached in one or two hours the resistance had fallen to only

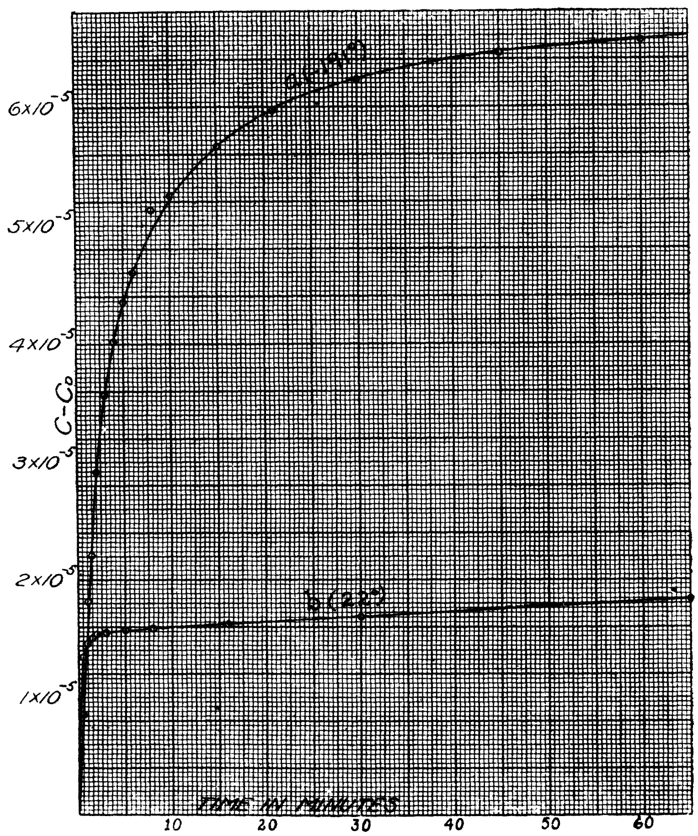

Fig. 6.

Variation in rate of saturation at different temperatures. Cell XVII. Excitation by red light through aperture 0.6 cm. in diam. Initial dark resistances: *a*, 4×10^8; *b*, 40,600.

a few thousand ohms. The circular opening for the admission of light was then closed and the cell left to recover the normal dark resistance. At frequent intervals the resistance was noted. Recovery was found to be extremely slow and in no instance was it found practicable to prolong the experiment sufficiently to bring the resistance of the cell anywhere nearly back to the value before

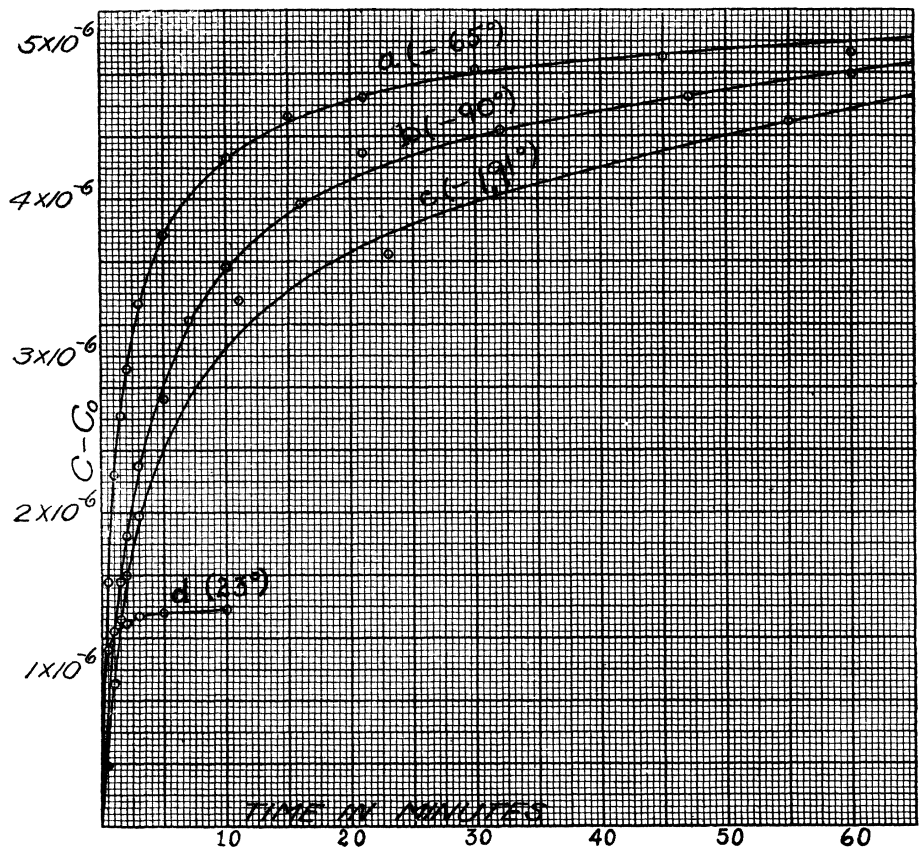

Fig. 7.

Variation in rate of saturation at different temperatures.[1] Cell XXI. Excitation by white light through aperture 0.9 cm. in diam. Initial dark resistances: *a*, 3.6×10^6; *b*, 9×10^6; *c*, 6×10^7; *d*, 292,000.

[1]Additional points were located as follows:
a, 1°15′, .000005041; *b*, 1°15′, .000004991; *c*, 1°13′, .000004791. It is to be noted that the curves extend very nearly to a point where the lower curves would cross the upper, thus indicating the probability that the change produced by saturation increases with decrease in temperature even at temperatures approaching that of liquid air.

excitation. Twenty-four hours after the conclusion of the experiment the dark resistance of the cell at room temperature was found to be somewhat higher than before the experiment. For the experiments at other temperatures the same method was followed.

From the data obtained there were plotted recovery curves in which, as before, the reciprocal square roots of the changes in conductivity were plotted against the times (see Figs. 4–5) and saturation curves in which the changes in conductivity during excittation were plotted against the times (see Figs. 6–7). A study of these curves leads to the conclusion that the recovery at low temperatures follows the same general laws as that at ordinary temperatures. The greater the initial effect produced the slower is the recovery. Compared with the recovery at ordinary temperatures the recovery at liquid air temperatures is extremely slow, and this change in the rate of recovery is greater than would be brought about merely by the increase in the initial effect produced (see Figs. 4–5).

As the temperature decreases change in conductivity upon exposure to light takes place more slowly; saturation is not reached so quickly but the change produced by complete saturation increases as the temperature decreases (see Figs. 6–7). Hence the change in conductivity produced by excitation of the same intensity and duration may be either greater or less at low temperatures than at ordinary temperatures. For excitations of slight intensity and short duration the change in conductivity will be less at low temperatures, but as the intensity or duration of excitation increases the ratio of the change at liquid air temperature to that at room temperature increases. The values of this ratio for the initial points of curves *a* and *b*, *c* and *d*, *e* and *f*, Fig. 4, are respectively 33 per cent., 56 per cent. and 476 per cent. Furthermore, since the initial dark conductivity at liquid air temperature is so nearly zero the ratio of change in conductivity to the initial conductivity is enormously greater than at ordinary temperatures.

SUMMARY.

The results of the investigation may be briefly summarized as follows:

1. The action of light and heat in producing change in the conductivity of selenium is apparently identical.

2. The increase in resistance with decrease in temperature continues down to the temperature of liquid air where the cell becomes almost entirely non-conducting.

3. Change in conductivity due to excitation by light of the same intensity takes place more slowly at low temperatures than at ordinary temperatures, but the final change produced by saturation is enormously greater.

4. Recovery at low temperatures is markedly slower than at ordinary temperatures.

This investigation was carried out during the summer of 1909 in the Physics Laboratory of Cornell University, and in conclusion the writer desires to express her thanks to Professors Merritt and Shearer for their many helpful suggestions.

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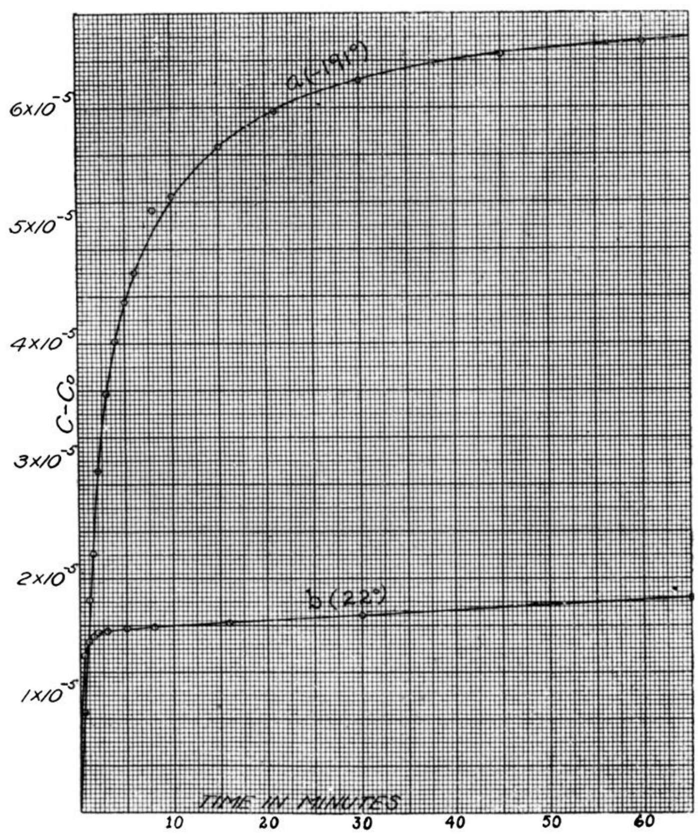

Fig. 6.

Variation in rate of saturation at different temperatures. Cell XVII. Excitation by red light through aperture 0.6 cm. in diam. Initial dark resistances: *a*, 4×10^8; *b*, 40,600.